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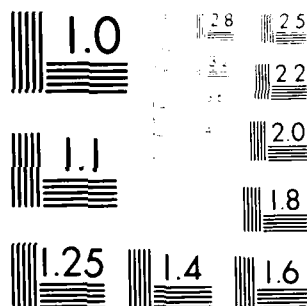
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TECHNICAL REPORT NO. 21

An Infrared Study of  
Ambient Temperature Chloroaluminates  
as a Function of Melt Acidity

by

Stephen Tait and Robert A. Osteryoung

Prepared for Publication

in

Inorganic Chemistry

Department of Chemistry  
State University of New York at Buffalo  
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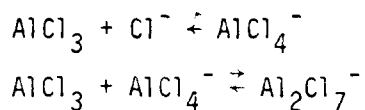
ABSTRACT

The infrared spectra of butyl pyridinium chloride/aluminum chloride and 1-methyl 3-ethyl imidazolium chloride/aluminum chloride room temperature molten salts have been examined over a range of mole ratios (acidities). Bands observed in the  $4000\text{-}630\text{ cm}^{-1}$  range have been assigned and spectral changes attributed to the formation of ion pairs, which may involve distortion of the aromatic ring since there is an accompanying loss of aromatic character. This effect is more pronounced in the imidazolium melts where more highly basic melts can be studied due to the greater liquidus range. Several isobestic points are reported.

Addition of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  to imidazolium melts gave rise to distinct new features in the spectra. In an acidic melt a new spectrum emerged after spectral subtraction which is believed to be due to the formation of either  $\text{AlO}(\text{OH})$  or, more likely,  $\text{AlOHCl}_2$ . Addition of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  to a basic melt gave a complex spectrum.

## INTRODUCTION

Until recently it has been accepted that melt equilibria in N-(1-butyl)pyridinium chloride (BuPyCl)/aluminum chloride ( $\text{AlCl}_3$ ) and the 1-methyl 3-ethyl imidazolium (ImCl)/aluminum chloride room temperature melts can be described by the two equilibria (1):



The former is dominant in basic melts i.e. where the  $\text{AlCl}_3$ :BuPyCl mole ratio is less than 1 and the latter in acid melts where the ratio is greater than 1. The role of the cation had been ignored until Wilkes et al (2) and Popov (3) undertook NMR studies of this molten salt system (2,3) and of a similar 1-methyl 3-ethyl imidazolium chloride (ImCl) system (2). Both provided good evidence of ionic interaction (particularly on the basic side) and Wilkes et al proposed several oligomers to explain the observed behavior.

This problem has not been studied by IR spectroscopy due to the highly corrosive nature of the melts, the lack of resistant, wide transmission windows and the inability to compensate for the large molten salt absorbances encountered even in short pathlength cells. The recent acquisition of an FTIR spectrometer and the development of a transmission cell with silicon windows (a configuration thought to possess severe disadvantages) (4,5) has minimized these problems.

In this work the mid IR spectra of both the BuPyCl and ImCl/ $\text{AlCl}_3$  melts have been studied as a function of acidity in order to examine the nature of the ionic interaction more closely. Water has also

been added to the melt in an attempt to find out more about the "aging" process in melts and the initial results are reported.

## EXPERIMENTAL

The experimental details below have been compiled in accordance with the criteria laid down by a sub-committee of the Coblenz society for the comparison of computerized infrared spectra (6).

### Instrument Information

The spectrometer was manufactured by Nicolet, Model 7199 and was used in unmodified form exclusively for transmission spectroscopy. The detector was a nitrogen cooled mercury-cadmium-tellurium detector (range  $400\text{--}5000\text{ cm}^{-1}$  - noise equivalent power of  $2 \times 10^{-10}\text{ W/hz}^{1/2}$ ). The detector element had an area of  $1\text{ mm}^2$ . The source was a water-cooled Globar and the beam splitter was germanium on a potassium bromide substrate (range  $400\text{--}4000\text{ cm}^{-1}$ ).

### Data Collection

A Happ-Genzel apodization function was applied to the double-sided interferogram. The collection parameters used to obtain spectra at a resolution of  $1\text{ cm}^{-1}$  are shown in Table 1. The times quoted include mirror return and acceleration to constant velocity but not the pre-collection beam equilibration delay.

Data collection, spectral subtraction and plotting of spectra were automated using the macro programming system developed in this laboratory.

### Sampling Data

The dynamic range of the ADC was 15 bits and the word length



was 20 bits. A system of gain-ranging was used in the collection program which changed the sensitivity away from the center burst of the interferogram to allow detection of small signals.

#### Spectral Manipulation

For clarity of presentation smoothing has sometimes been used in spite of the fundamental objection raised by Grasselli et al (6) that band degradation occurs when data collected on an FTIR are smoothed. Spectra were, however, checked to see that significant absorbance peaks were neither created nor removed by this operation. Values for peak frequency and absorbance were taken from unsmoothed data. An 11 point 2nd order Savitsky-Golay algorithm was used for smoothing. The absorbance values found after subtraction of the empty cell were corrected for movements of the baseline caused by the different refractivities of the filled and empty cell.

No attempt was made to automatically remove water vapor absorbances from spectra. The region near  $1650\text{ cm}^{-1}$  containing the sharpest absorbances for this purpose was obscured by absorbances attributable to the melt and small changes in the background were large relative to the water absorbance near  $3500\text{ cm}^{-1}$ . Since the instrument was kept in an area of controlled low humidity and was continuously purged with nitrogen this was not a significant problem. Water or carbon dioxide bands could have led to confusion the instrument was purged for 15 minutes before spectra were run.

#### Sampling Accessories

All sampling accessories were supplied by Harrick Scientific Corporation. The cell consisted of a stainless steel body with a

teflon insert (see Figure 1). The cell windows were 13 mm in diameter and 2 mm wide polished silicon discs and were separated by half-moon spacers of 0.05 mm thickness. The assembly was screwed down to align the cell windows with the entrance and exit to the teflon plugs. The molten salts flowed through these hollow threaded plugs without contacting the stainless steel.

When the windows were kept parallel by the use of two spacers, 5 separate lagged interferograms were observed due to reflection, which transformed to give fringes (Figure 2). The unwanted interferograms could be removed in an empty cell by generating a straight line across the sections of the interferogram where the fringes occurred; however, in the presence of melts this led to distortion of the sample spectrum.

When the windows were tilted with respect to each other by using only one spacer (see Figure 3), the lagged interferograms disappeared and a flat baseline resulted on transformation (see Figure 2). The cell was maintained in this configuration for all samples; the procedure adopted for filling and emptying the cell is detailed below. The nominal cell pathlength was 0.025 mm and the cell volume was 6.3  $\mu$ l. The pathlength of the cell was checked with the windows parallel using two spacers by measuring the frequency difference between fringes and the cell pathlength was found to be accurate to  $\pm 5\%$ .

The cell was filled using a 1 ml tuberculin syringe in a Vacuum Atmospheres Drybox maintained at <5 ppm oxygen and water by a Vacuum Atmospheres HE193/2 Dritrain purification system which circulated the box atmosphere through molecular sieves and a copper catalyst

bed to remove oxygen. The cell was angled to avoid trapping bubbles between the opaque silicon windows during filling and sealed with teflon stoppers. The cell was emptied without disassembly by slowly flushing with 5 ml of methylene chloride to remove the molten salt, 10 ml of methanol to dissolve any residual films and finally with 5 ml methylene chloride to remove the methanol. The cell was then flushed with argon and dried in vacuo for at least 20 minutes before being refilled with the next sample.

#### Chemicals

Anhydrous aluminum chloride (Fluka AG) was distilled once under vacuum in a sealed Pyrex tube from a mixture containing sodium chloride and aluminum wires. This procedure and the preparation of butyl pyridinium chloride (BuPyCl) has been described elsewhere (7).

Preparation of 1-methyl, 3-ethyl imidazolium chloride (ImCl) was based on a method described by Wilkes et al (8) using a pressure bottle assembly manufactured in our workshop. Following the reaction, a white precipitate formed on cooling and the residual ethyl chloride was vented. Since the product was highly hygroscopic (recrystallization on the open bench result in the formation of oils) it was dissolved in hot acetonitrile in a closed glassware apparatus and recrystallized by the addition of cooled ethyl acetate. Seeding assisted recrystallization. After two recrystallizations the product (mp 82-86°C) was filtered, dried under vacuum at room temperature and transferred to the drybox for storage.

## RESULTS AND DISCUSSION

In previous studies (9) polyethylene had been used as the cell window material for IR work on similar molten salts because of its low background absorbance and inertness to the melt; however it does absorb strongly in the C-H stretching region ( $2800-3000\text{ cm}^{-1}$ ) and its flexibility makes a fixed pathlength cell more difficult to obtain. Silicon windows were selected for this work as they appeared to be resistant to corrosion by melts of any acidity, could be arranged to give a reproducible cell pathlength and provided a wider transmission window.

The disadvantage of using silicon is its high refractive index which leads to high background absorbances ( $\sim 0.75$  abs units). In addition the spectrum of silicon ( $607-602$  and  $626-612\text{ cm}^{-1}$ ) and of its impurities (carbon  $607-602\text{ cm}^{-1}$  and oxygen  $1125-1090\text{ cm}^{-1}$ ) also interfere (10); however, since the melt does not interact with the windows, all but the major silicon absorbance at  $620\text{ cm}^{-1}$  (i.e., absorbances less than 2 abs units) can be subtracted without any alteration to the sample spectrum. Where the absorbance exceeds 2 abs units (i.e. less than 1% transmission) subtraction becomes less accurate and the result is a confused differential. This work has, therefore, been restricted to the  $4000-630\text{ cm}^{-1}$  range.

Melt spectra were recorded over a range of acidity from 0.8:1 to 2:1  $\text{AlCl}_3/\text{BuPyCl}$  and 0.4:1 to 1.75:1  $\text{AlCl}_3/\text{ImCl}$ . In order to compare melts of different acidity the spectra were corrected for cation dilution by multiplying the spectra by a correction factor after the background

cell window spectrum had been subtracted. The molar cation concentration is given by:

$$[R^+] = \frac{\text{Mole fraction}_{\text{RCl}} \cdot \text{Density} \times 10^3}{\text{Binary Molecular Weight}}$$

where  $R^+$  = butyl pyridinium or imidazolium cation and the binary molecular weight is given by:

$$\text{Binary Molecular Wt.} = [(\text{Mole fraction}_{\text{AlCl}_3} \cdot \text{Mol. Wt.}_{\text{AlCl}_3}) + (\text{Mole fraction}_{\text{RCl}} \cdot \text{Mol. Wt.}_{\text{RCl}})]$$

The correction factor is the ratio of the cation concentration in a particular melt to the cation concentration in a 0.8:1  $\text{AlCl}_3/\text{BuPyCl}$  for  $\text{BuPyCl}$  melts or in a 0.4:1  $\text{AlCl}_3/\text{ImCl}$  for  $\text{ImCl}$  melts (see Table 2) (11). Thus, any absorbances unaltered by changes in melt acidity after correction are inferred to be due to vibrations which are not affected by melt interactions.

#### IR Spectra of $\text{AlCl}_3/\text{BuPyCl}$ Melts

The IR spectrum of an empty cell alone and filled with 0.8:1  $\text{AlCl}_3/\text{BuPyCl}$  melt are shown in Figure 4. The subtraction of these two spectra and a similar subtraction for a 1.8:1  $\text{AlCl}_3/\text{BuPyCl}$  melt are shown in Figure 5. The peak frequencies and absorbances of the two melts are detailed in Table 3 and compared with the same data for the methyl pyridinium cation (12).

As expected there are both similarities and differences, most of the latter attributable to the presence of the butyl group. There is increased aliphatic C-H stretching ( $2850\text{-}3000\text{ cm}^{-1}$ ), C-H/C-N mixed out of plane bending modes ( $1347\text{-}1454\text{ cm}^{-1}$ ), C-N stretching ( $1251\text{ cm}^{-1}$ ), aromatic C-H in plane bending ( $950\text{-}1230\text{ cm}^{-1}$ ) and C-H bending at

$686\text{ cm}^{-1}$ . The last band only occurs strongly where there are at least 4 adjacent methylene groups in the alkyl chain (13).

The spectra of acidic and basic melts were very similar. Many of the bands were sharp in the acidic melt but broader in the basic melt (e.g.,  $1214$ ,  $1320$ ,  $1464$ - $1501$ ,  $1584$  and  $1634\text{ cm}^{-1}$ ) and peak frequencies were lower by between  $2$ - $6\text{ cm}^{-1}$ . Both the loss of symmetry suggested by the first effect and the peak shift are indicative of an interaction, perhaps ion pair formation, though the magnitude suggests that this is not a strong effect. Similar, and more pronounced effects are observed in the  $\text{ImCl-AlCl}_3$  melts (see below) where studies could be performed in more basic melts.

The absorbance change in intensity (9) at  $1450$ - $1500\text{ cm}^{-1}$  in acidic melts found by Gale and Osteryoung was observed but the bands at  $1256$  and  $1360\text{ cm}^{-1}$  could not be reproduced. This may indicate that polyethylene windows employed in this earlier study were not inert to attack by acidic melts.

The main difference between acidic and basic melts was in the C-H stretching region. A new broad band emerged at  $3018\text{ cm}^{-1}$  as the melt was made basic (see Figure 6). A similar band appears in the  $\text{ImCl}$  melts (see below), but the source of this band is not known.

In spite of the interference caused by this effect it appears that the intensities in the aliphatic C-H stretching region at  $2970$ - $2870\text{ cm}^{-1}$  are enhanced and that the intensities of C-H aromatic bands at  $3130$ - $3070\text{ cm}^{-1}$  are diminished as the acidity decreases. These changes indicate a loss in ring aromaticity, which has also been observed by NMR where proton chemical shifts tend toward those expected of a conjugated alkene as melts are made more basic (2,14).

Further differences arise in the  $660\text{--}840\text{ cm}^{-1}$  region (see Figure 7). A multi peaked band was observed at  $773\text{ cm}^{-1}$  in a 1.2:1  $\text{AlCl}_3/\text{BuPyCl}$  melt with a shoulder at  $782\text{ cm}^{-1}$ . The area of the band decreased with increasing acidity or basicity from a neutral melt (spectra could not be obtained in the neutral region itself as the melt solidified at room temperature). The band shape also distinctly altered and the peak altered to  $772\text{ cm}^{-1}$  in 0.8:1  $\text{AlCl}_3/\text{BuPyCl}$  and  $768\text{ cm}^{-1}$  in 2:1  $\text{AlCl}_3/\text{BuPyCl}$  melt. The shoulder at  $782\text{ cm}^{-1}$  remained unaltered.

A large off-scale absorbance at  $670\text{--}695\text{ cm}^{-1}$  varied in intensity in the same way but was only on-scale in the 2:1  $\text{AlCl}_3/\text{BuPyCl}$  melt. The band consisted of a broad absorbance at  $691\text{ cm}^{-1}$  with two peaks superimposed on it at  $686$  and  $683\text{ cm}^{-1}$ . The absorption bands in this region were, however, very large.

The vibrational modes of pyridine assigned by Spinner (12) were based on the degenerate vibrational modes of benzene described by Lord et al (15). The aromatic out of plane modes are assigned to the  $772\text{ cm}^{-1}$  and  $683\text{ cm}^{-1}$  bands.

Association by the cation with species above or below the plane of the molecule (i.e., ion pairing) might reduce the intensity of the vibration. The  $683\text{ cm}^{-1}$  band is more affected than the  $772\text{ cm}^{-1}$  band. This postulated association is consistent with the observation of Wilkes et. al. (2) in NMR studies on these molten salts.

In summary, the change in band shape and intensity as the melt acidity is varied across the range suggest that intermolecular interaction, perhaps ion pair formation, is taking place in both the acidic and basic melts. Loss of aromaticity in the basic melts suggest that there may be some ring distortion associated with this interaction.

#### IR Spectra of $\text{AlCl}_3/\text{ImCl}$ Melts

Infrared spectra for the 0.4:1  $\text{AlCl}_3/\text{ImCl}$  and 1.5:1  $\text{AlCl}_3/\text{ImCl}$  melts with silicon cell window absorbance subtracted are shown in Figure 8. The peak frequencies and absorbances for these two melts and for ImCl in methylene chloride are tabulated and assigned in Table 4. The same data for liquid imidazole is also included to differentiate bands which could be attributable to either the organic cation or inorganic species. The spectra have all been corrected for changes in cation concentration as before (see Table 2).

Imidazole has been the subject of several IR studies (16,17) and the spectrum is complicated by coupled vibrations arising from the heterocyclic ring and by considerable N-H...N association effects. In addition the position of bands is known to move when the ring positions are substituted (18) though 1,3 substitution removes N-H association.

In general, many of the bands found in the melt are in a similar position to those found in imidazole, but shifted to lower frequencies due to the inductive effect of the alkyl groups. Bands have been assigned on the basis of peak position, intensity and sensitivity to ring substitution relative to imidazole and its derivatives (19). The spectrum of ImCl in methylene chloride is very similar to that of



the 0.4:1  $\text{AlCl}_3/\text{ImCl}$  basis melt but is different in acidic melts, which suggests interaction, perhaps the formation of ion pairs, in both methylene chloride and the basic melt. The broadening and shift of peaks observed in the BuPyCl melts occurred more strongly in the ImCl melts; the change in peak frequency and absorbance of the most sensitive bands are tabulated in Table 5. The changes in the basic melts were more marked than for BuPyCl since more basic melts are attainable, but there were only small alterations to the spectra over the acidic range. Thus specific interactions, perhaps ion pair formation, appear to be much stronger in the basic than in the acidic melt.

Differences between the acid and basic melts can be split into three regions 3600-1600, 1600-900 and 900-630  $\text{cm}^{-1}$ .

3600-1600  $\text{cm}^{-1}$

Virtually no change was observed as the melt acidity was altered from 2:1 to 1:1  $\text{AlCl}_3/\text{ImCl}$  and the resulting spectra were almost superimposable after correction for concentration changes (see Figure 9); thus Beer's law was obeyed for these melts down to at least 1% transmission, a fact which is most important in considering the changes taking place in the basic melts.

In the basic region there were considerable changes as the melt acidity was varied from 0.4:1 to 1:1  $\text{AlCl}_3/\text{ImCl}$  (see Figure 10). A broad band with peaks at 3052 and 3018  $\text{cm}^{-1}$  increased as the melt was made more basic and distorted the other bands in this region. The aromatic band at 3167  $\text{cm}^{-1}$  diminished considerably and the band at 3114  $\text{cm}^{-1}$  nearly disappeared under the 3052/3018  $\text{cm}^{-1}$  band. An isosbestic point occurs at 3103  $\text{cm}^{-1}$  indicating an interaction involving at least two

species whose concentrations vary with acidity. The aliphatic C-H stretching band at  $2993\text{ cm}^{-1}$  shifts to  $2982\text{ cm}^{-1}$  and the bands at  $2963$  and  $2943\text{ cm}^{-1}$  behaved similarly becoming indistinguishable from the broad bands at  $3052/3018\text{ cm}^{-1}$  in very basic melts.

As with the BuPyCl melt, the broad band at  $3052/3018\text{ cm}^{-1}$  varies with melt acidity in the basic region. Bands in a similar region have been studied in liquid imidazole by Bellocq et al (16) who attributed them to a hydrogen bond, HN--H association. They deuterated imidazole in the 1 position and shifted the part of this region responsible for this effect. The band position (assuming a value of  $\nu_{\text{N-H}}/\nu_{\text{N-D}}$  of 1.34), shape and intensity is similar to that seen in this melt. While recent studies support Bellocq's et al explanation of the breadth and complexity of the bands in this region observed in imidazole (19,20) the presence of the band in the ImCl melt, however, should not be due to similar interaction, since both of the nitrogen atoms are substituted, but there is no obvious source of available proton, except for perhaps traces of water, in the melt. This band could possibly be due to a hydrogen bond type of interaction between  $\text{Cl}^-$  and H on C-2 of the imidazole ring. (Note that a band in a similar region varies with acidity in the BuPyCl melt.) In acid melts this broad band is absent and in the basic melts its intensity is clearly a direct function of the chloride concentration. Since this band also occurs in the basic BuPyCl melts it is not a function of the imidazole ring but could be related to an aromatic ring nitrogen or, as mentioned above, to a hydrogen bond between chloride and hydrogen in the butylpyridinium or imidazolium cation.

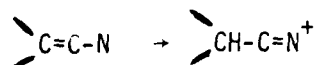
A broad low intensity absorbance in the 2600-2900  $\text{cm}^{-1}$  region in the neutral and acidic melts becomes enlarged in the basic region and peaks emerged at 2866, 2833(shoulder), 2750 and at 2677  $\text{cm}^{-1}$ .

In the 2600-1600  $\text{cm}^{-1}$  region the absorbances are small and have been assigned previously to non-fundamental modes, i.e. overtones or combination bands (19). The absorbance found at 1765  $\text{cm}^{-1}$  in 0.4:1  $\text{AlCl}_3/\text{ImCl}$  is absent in acidic melts. The band at 1660-1680  $\text{cm}^{-1}$ , which is observed in the 1.5:1  $\text{AlCl}_3/\text{ImCl}$  melt but obscured in the 0.4:1  $\text{AlCl}_3/\text{ImCl}$  melt is probably due to either an overtone of the 834  $\text{cm}^{-1}$  band and/or combination of the 1033 and 645  $\text{cm}^{-1}$  bands.

#### 1600-900 $\text{cm}^{-1}$

In addition to the general broadening and shifting of peaks already mentioned a shoulder on the 1570  $\text{cm}^{-1}$  peak emerges at 1590  $\text{cm}^{-1}$  (see Figure 11). This enlarges to a separate peak at 1595  $\text{cm}^{-1}$  in acidic melts and cannot be attributed to a combination band. The change in peak frequency and intensity is shown in Table 5.

Similar effects have been recognized in studies of  $\alpha\beta$ -unsaturated tertiary amines (21,22), where increases of peak frequency of 20-50  $\text{cm}^{-1}$  have been observed in going from an  $\alpha\beta$ -unsaturated amine (enamine) to its perchlorate salt corresponding to the transformation:



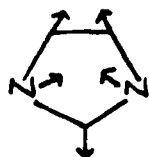
For instance, 1-n-butyl-2-methyl-tetrahydropyridine absorbs at 1649  $\text{cm}^{-1}$  in the base form and 1684  $\text{cm}^{-1}$  as the perchlorate salt. For

aromatic rings this structural change amounts to a loss of aromaticity and characteristics more similar to a conjugated tertiary amine. In the melts the shift between the acidic melt and the  $1570\text{ cm}^{-1}$  peak is  $25\text{ cm}^{-1}$ ; thus it appears that the I or III forms of the cation (see Scheme 1) have more significance as the chloride concentration is increased.  $900\text{-}630\text{ cm}^{-1}$  (Figure 12)

As for the BuPyCl melts the ring bending modes of vibration are the most sensitive to changes in melt acidity. The in plane ring bending band at  $834\text{ cm}^{-1}$  diminishes with little change in peak frequency as the acidity is reduced and is replaced by a very broad band ( $794\text{-}899\text{ cm}^{-1}$ ) in highly basic melts. Isosbestic points are observed at  $823$  and  $853\text{ cm}^{-1}$  as this change takes place. Subtraction in this region is less accurate than in higher wave number regions.

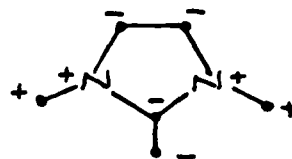
The out of plane bending mode at  $760\text{ cm}^{-1}$  shifts to higher frequencies and broadens significantly (see Table 5). The two modes of vibration are shown below (19) and it again appears that modes of vibration which distort the position of the ring nitrogen atoms are more sensitive to acidity changes. When this observation is linked

In plane ring bending



$834\text{ cm}^{-1}$

Out of plane C-H bending

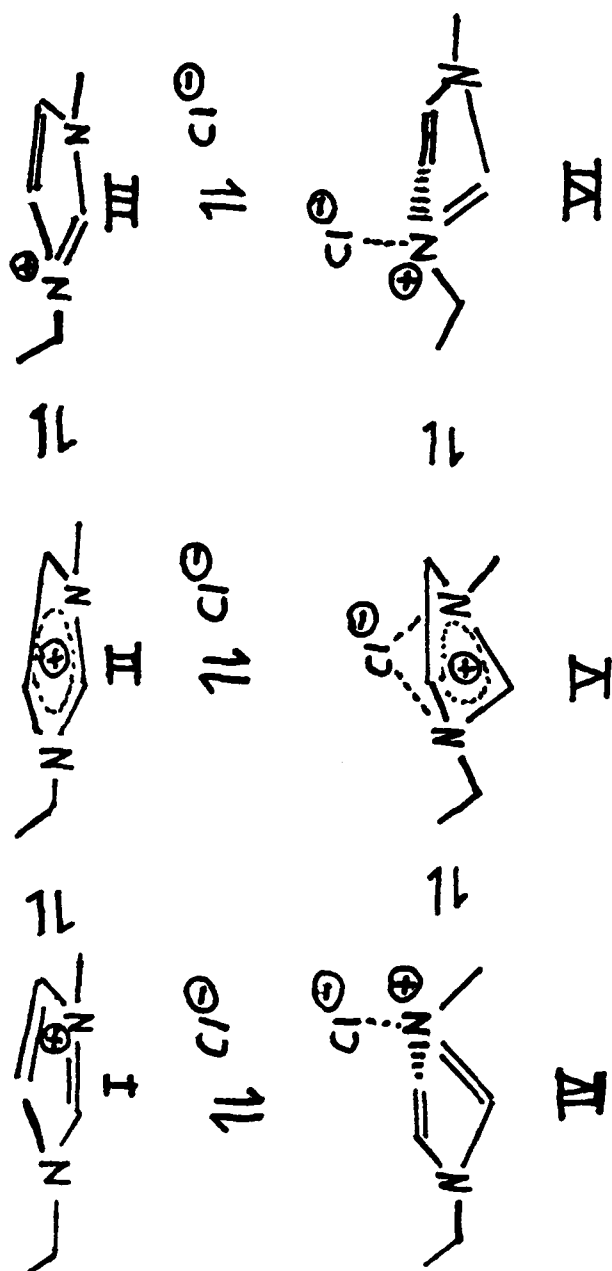


$760\text{ cm}^{-1}$

with the enamine effect, the loss of aromaticity and the electronic repulsion between the chloride ion and the  $\pi$  electrons of the ring, distortion of the ring is suggested. This is illustrated in Scheme 1.

Wilkes et al (2) have suggested on the basis of their nmr studies that ion interactions occur in the form of oligomeric chains held together by ion-ion interactions in the basic melts. Two chlorides or one chloride and one tetrachloroaluminate or two tetrachloroaluminates, presumably with one above and below the plane of the ring are postulated as species. Popov has postulated the existence of ion pairs in the  $\text{BuPyCl-AlCl}_3$  melt, also on the basis of nmr work (3). The results presented above, particularly with regard to the isosbestic point appearance and variation with acidity, appear to lend support to a two-species - i.e., ion pair - interaction. It is possible that whatever specific interaction takes place giving rise to the isosbestic point(s) depends only on whether or not the closest neighbor to the imidazolium ring is a single chloride ion; the formation of an oligomer by some time averaged proximity of a second chloride to the initial  $\text{BuPy}^+/\text{Im}^+\text{Cl}^-$  "ion pair" may not result in additional perturbations sufficient to result in further IR spectral changes.

The frequency at  $703\text{ cm}^{-1}$  could not be assigned to a cation vibration (unless it is the aliphatic C-H bending mode, which is unlikely (13)) and it increased in size without any change in peak frequency as the melt acidity was increased. Since Al-O stretching bands are known to exist in this region (23,24), the possibility that this was linked to the "aging" of melts was examined by adding water.



### Addition of Water to $\text{ImCl}/\text{AlCl}_3$ Melts

#### 1.6:1 $\text{AlCl}_3/\text{ImCl}$ Acid Melt

Acidic melts react with water in a highly exothermic manner with the evolution of hydrogen chloride and the formation of a white precipitate. This redissolves on stirring and the spectrum of this melt (20 mM water) after subtraction of a reference 1.6:1  $\text{AlCl}_3/\text{ImCl}$  melt spectrum is shown in Figure 13. The same spectrum for the addition of  $\text{D}_2\text{O}$  is shown in Figure 14. The peak frequencies are compared in Table 6 with other aluminosy species.

The subtracted spectrum only contains three bands at 3323, 1119 and  $703\text{ cm}^{-1}$ , which increase linearly in magnitude with further additions of water. Both the 3323 and  $1119\text{ cm}^{-1}$  bands disappeared when  $\text{D}_2\text{O}$  was added (60 mM) (apart from some traces of water in the  $\text{D}_2\text{O}$ ) and new bands were found at 2477 and  $853\text{ cm}^{-1}$ . The ratio of the two bands in each case was close to the theoretical shift of 0.76 and the bands were assigned to O-H stretching and O-H bending respectively. These bands are typical for an inorganic compound containing a hydroxy group (23). The  $703\text{ cm}^{-1}$  band shifts by only a factor of 0.94 and was assigned to an Al-O-H stretching mode. A similar band is found in the spectra of aluminum oxide, aluminum hydroxide (see Table 6) and chloroaluminosy species (24-26) though studies on the latter were obtained in aqueous media where the coordination of water and the formation of dimers complicate the spectrum. The absence of any Al-O-Al absorbances which typically occur near  $2400\text{ cm}^{-1}$  (e.g., as in aluminum oxide) indicate that dimers are not formed in the acidic melt (25). Since the spectrum shows

no dimers the initially insoluble material must be dissolving up as a monomeric species such as  $\text{AlO}(\text{OH})$ ,  $\text{Al}(\text{OH})\text{Cl}_2$  or  $\text{Al}(\text{OH})_2\text{Cl}$ .

A study by Moolenaar et al (24) showed that a dihydroxy anion  $\text{AlO}(\text{OH})_2^-$  has absorbances at 900, 705 and  $540\text{ cm}^{-1}$ . By analogy  $\text{Al}(\text{OH})_2\text{Cl}$  becomes unlikely as only one of the two possible bands visible in the transmission range is observed. Differentiating between  $\text{AlO}(\text{OH})$  and  $\text{Al}(\text{OH})\text{Cl}_2$  is difficult as the IR region below  $600\text{ cm}^{-1}$  is obscured by melt and window absorbances which prevent a search for the presence of Al-Cl stretching or dihydroxy antisymmetric bending modes. Of the two species the  $\text{AlOHCl}_2$  is the more probable as the hydrogen atom on  $\text{AlO}(\text{OH})$  would be shared leading to shifted peak frequencies and broader bands. In addition, previous electrochemical studies (1,27) suggested that  $\text{AlOCl}$  was the aluminosy species arising in acid melt when oxide was added and  $\text{Al}(\text{OH})\text{Cl}_2$  is closer to this than  $\text{AlO}(\text{OH})$ .

Further additions of water to the melt led to the emergence of other bands in the spectrum (a broad multi-peaked band centered at  $2175\text{ cm}^{-1}$  and another at  $1230\text{ cm}^{-1}$ ) possibly indicating the presence of other species at higher concentrations of added water.

#### Addition of Water to a 0.4:1 $\text{AlCl}_3/\text{ImCl}$ Melt

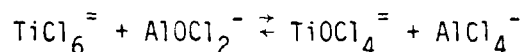
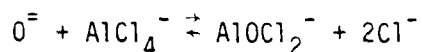
Water (60 mM) reacted slowly with the basic melt to give a white precipitate which redissolved on stirring. (Not all of this precipitate redissolved when water was added to an approximately neutral melt.) The IR spectrum of the melt and redissolved precipitate after subtraction of a reference 0.4:1  $\text{AlCl}_3/\text{ImCl}$  melt was complex, but showed similarities with spectra obtained by Riesgraf and May (26), who added freshly



prepared aluminum hydroxide gels to aluminum chloride solutions. At least three bands were observed in the O-H stretching region (3520(?), 3350, 3100  $\text{cm}^{-1}$ ) and two in the O-H bending region (1180, 1190  $\text{cm}^{-1}$ ). The remaining bands in the spectrum are weak and/or broad, though similarities exist between this spectrum and that of Riesgraf and May (26). On addition of  $\text{D}_2\text{O}$  (60 mM) the bands assigned to the hydroxyl group all shifted to lower frequencies by a factor close to 0.76 as before.

Recent work suggested that water reacts to form  $\text{HCl}$  and some unknown aluminum hydroxy species (28).

The formation of an  $\text{Al-OH}$  species in the chloroaluminate melt explains some of the results obtained during an electrochemical study of oxide and water addition in a basic  $\text{BuPyCl}/\text{AlCl}_3$  melt in the presence of  $\text{Ti(IV)}$  (1). Two  $\text{Ti(IV)}$  reduction waves were found which varied with oxide concentration as a result of the equilibria:



the latter equilibrium being quite slow. The addition of water shifted the  $\text{Ti(IV)}$  equilibrium to the left, indicating that water acted to remove  $\text{AlOCl}_2^-$ . The formation of an  $\text{Al-OH-Cl}$  species would account for the observed chemistry.

Table 1

Spectrometer Settings for Data Collection at  $1 \text{ cm}^{-1}$  Resolution

<u>Data collection</u>	
# of data points / interferogram	16384
# of transform points	32768
# of data points before centre burst	256
High pass filter (hz) equivalent to a cut-off at $85 \text{ cm}^{-1}$	100*
Low pass filter (Khz) equivalent to a cut-off at $8530 \text{ cm}^{-1}$	10*
<u>Scanning measurements</u>	
# of scans	1000
Pre-collection beam delay (secs)	5
Total measurement time (secs)	1561
Scanning time (secs)	885
Mirror velocity (mms retardation/sec)	11.72
Retardation between points (mms)	$6.86 \times 10^{-4}$

\* This is the nominal roll-off frequency (3dB down point) of a Butterworth high/low pass noise filter

Table 2

## IMIDAZOLIUM CHLORIDE/ALUMINUM CHLORIDE MELTS

Cation Concentration Correction Factors for the Normalization of BuPyCl and ImCl Melt Spectra

Mole Ratio ( $\text{AlCl}_3/\text{ImCl}$ )	Melt Density (gm/cc)	Mole Fraction ImCl	Binary Melt Molecular Wt.	Cation Conc'n (Moles/litre)	Correction Factor
0.4	1.21	0.71	142.8	6.02	1.0
0.55	1.23	0.65	142.0	5.63	1.07
0.7	1.25	0.59	141.1	5.22	1.15
0.85	1.27	0.54	140.5	4.88	1.23
0.95	1.28	0.51	140.1	4.66	1.29
1.0	1.28	0.50	140.0	4.57	1.32
1.25	1.31	0.44	139.2	4.22	1.43
1.5	1.34	0.40	138.7	3.87	1.56
1.75	1.35	0.36	138.1	3.52	1.71
2.0	1.38	0.33	137.7	3.31	1.82

## BUTYL PYRIDINIUM CHLORIDE/ALUMINUM CHLORIDE MELTS

Mole Ratio $\text{AlCl}_3/\text{BPC}$	Melt Density (gm/cc)	Mole Fraction BuPyCl	Binary Melt Molecular Wt.	Cation Conc'n (Moles/litre)	Correction Factor
0.8	1.22	0.56	154.8	4.41	1.0
0.85	1.23	0.54	154.0	4.31	1.02
0.9	1.23	0.53	153.6	4.24	1.04
0.95	1.24	0.51	153.0	4.13	1.07
1.25	1.28	0.44	150.2	3.75	1.17
1.5	1.30	0.40	148.7	3.50	1.26
1.75	1.32	0.36	147.1	3.23	1.36
2.0	1.33	0.33	146.0	3.00	1.47

1. Extrapolated or interpolated from data by Wilkes et al (11).

TABLE 3

Band Assignment	Methyl pyridinium iodide crystal		0.8:1 AlCl <sub>3</sub> /BuPyCl		1.8:1 AlCl <sub>3</sub> /BuPyCl	
	Reak Freq	Abs	Reak Freq	Abs	Reak Freq	Abs
Ar C-H str	3134	0.1	3134	0.41	3132	0.27
Ar C-H str/be	3118	0.1	3121	0.32		
	3081	0.05	3090	0.58	3091	0.47
Ar C-H str as	3074	0.25	3078	0.54		
	3056	0.1	3054	0.43	3048	0.08
	3038	0.45				
N-H str ass'n			3018	0.31		
Me C-H str as	2990	0.15	2967	1.15	2968	0.81
Me C-H str sym	2967	0.05	2940	0.91	2938	0.57
Aliph C-H str			2906	0.52		
"			2878	0.78	2879	0.49
"			2870	0.64	2870	0.30
Arom C-C str	1632	0.8	1634	0.87	1634	1.01
"	1581	0.15	1583	0.22	1584	0.16
Arom str/def	1501	0.8	1501	0.70	1501	0.78
"	1486	0.9	1488	1.14	1489	1.42
Comb 681/783			1464	0.70	1466	0.60
Me C-H as be	1444	0.1	1444	0.38		
Me C-H as be	1419	0.05				
Me C-H sym be			1384	0.33	1384	0.21
Ring be i/p sym	1347	0.01	1350	0.25	1352	0.14
"	1318	0.03	1320	0.38	1320	0.24
"	1287	0.3	1285	0.30	1285	0.14
"	1224	0.15	1251	0.24	1251	0.10
Ring be i/p as	1210	0.3	1214	0.35	1214	0.18
	1189	0.7	1175	0.77	1176	0.89
	1150	0.15				
C-H be i/p	1135	0.25	1118	0.23	1118	0.20
C-H be i/p	1057	0.20	1064	0.24	1064	0.17
I/p str as	1025	0.1	1029	0.18	1029	0.09
Ring be o/p	954	0.1	955	0.20	956	0.18
Ring be o/p as	868	0.05				
Ring be i/p as	800	0.02			818	0.16
Me C-H be ?			783	0.55	781	0.55
Ring be o/p as	773	0.70	772	1.14	768	1.31
"	771	0.79	738	0.21	735	0.24
Ring be o/p sym						
CH <sub>2</sub> be	678	0.9	686	4.0	681-686	4.0

1. Absorbance values have been corrected for non-zero baseline error arising out of the difference in refractive index of the cell empty and filled with melt.

Comparison of the IR spectra of 0.8:1 and 1.8:1 AlCl<sub>3</sub>/BuPyCl melts with the methyl pyridinium iodide

TABLE 4

Band Assignment	0.4:1 AlCl <sub>3</sub> /ImCl <sub>3</sub> N		1.5:1 AlCl <sub>3</sub> /ImCl <sub>3</sub> Me-1b		0.5M ImCl <sub>3</sub> in CH <sub>2</sub> Cl <sub>2</sub>		Imidazole (19)	
	Peak Freq	Abs	Peak Freq	Abs	Peak Freq	Abs	Peak Freq	
Arom C-H str	3148	0.57	3167 3122 310	1.0 0.87 0.73	3145	0.1	3124 3105	
N-H/O-H ass'n	3052 3018	1.22 1.20			3074 3039	0.18 0.30	3021	
Aliph C-H str	2982	1.38	2993 2963 2943	0.36 0.25 0.20	2999	0.25		
N-H ?	2866	0.48			2956 2865	0.42 0.14		
HCl ?	2833	0.28					2800	
N-H ?	2749	0.09			2730	0.04	2587	
HCl ?	2677	0.02			1732	0.05		
N-H ass'n	1764	0.13	1678	0.10				
Comb			1594	0.90				
C-C=N <sup>+</sup> -					1587	0.09	1573	
Comb	1569	1.22	1569	1.42	1573	0.22	1541	
Ring str sym	1464	0.60	1469	0.80	1467	0.11	1490	
"	1458	0.60	1454	0.68	1454	0.09	1450	
Me C-H be as	1427	0.38	1428	0.51	1428	0.08		
"	1389	0.35	1390	0.39	1388	0.08		
Ring str sym	1355	0.32	1357	0.39	1355	0.07	1323	
Me C-H be sym	1344	0.32	1344	0.41	1343	0.09		
Ring str sym	1336	0.44	1336	0.42	1337	0.09		
Ring C-H be sym	1302	0.20	1292	0.13	1302			
N-H i/p be	1252	0.17	1246	0.16	1178	0.37	1260 1242	
Ring str sym	1179	1.50	1167	2.54			1140	
Ring C-H i/p be	1108	0.22	1108	0.50	1099		1099	
Ring C-H i/p be	1080	0.31	1090	0.35	1052 972		1052 972	
Comb	1027-1033	0.17			1037	0.07		
N-H i/p be /C-H i/p be	959	0.16	959	0.14	959	0.02	934	
Ring i/p be	794-399				896	0.08	894	
C-H i/p be							835,827	
Ring o/p be as		0.29					756,736	
"	761	0.35	749	1.22	750	*		
Al-O str	704	0.09	703	0.3				
Ring be as	651	0.53	645	0.85	650	*	657	
Ring be as	617-631	> 8.0 **	618-630	> 8.0 **		*	619	

sym - symmetric as - asymmetric i/p - in plane o/p - out of plane str - stretching; be - bending

\* - obscured by C-Cl stretching absorbance \*\* combined with 91 cell window absorbance

Comparison of the IR spectra of 0.4:1 and 1.5:1 AlCl<sub>3</sub>/ImCl<sub>3</sub> melts, 0.5M IC in methylene chloride and liquid imidazole

Table 5

Comparison of Peak Frequency and Intensity Changes Occurring with Melt Acidity

Mole Ratio $\text{AlCl}_3/$	Arom C-H stretch		Aliph C-H stretch		-C=N- stretch		Ring stretch		Ring i/p bending		Ring o/p bending	
	Peak Freq.	Abs	Peak Freq.	Abs	Peak Freq.	Abs	Peak Freq.	Abs	Peak Freq.	Abs	Peak Freq.	Abs
0.40:1	3148	0.63	2981	1.43	1590	0.29	1178	1.48	834	0.34	760	0.46
0.55:1	3154	0.73	2983	1.25	1590	0.38	1175	1.44	838	0.45	758	0.60
0.70:1	3156	0.85	2985	1.05	1591	0.48	1172	1.55	837	0.58	754	0.84
0.85:1	3157	0.90	2987	0.76	1592	0.64	1170	1.98	837	0.76	751	1.04
0.95:1	3158	1.08	2988	0.52	1592	0.67	1168	1.57	837	0.95	747	1.05
1.0:1	3159	1.02	2990	0.40	1595	0.72	1170	1.87	838	1.19	747	1.20
1.20:1	3159	0.98	2991	0.40	1595	0.71	1169	2.15	837	1.09	747	1.30
1.50:1	3161	1.00	2992	0.39	1595	0.78	1169	2.14	836	0.98	747	1.42
1.75:1	3161	1.03	2993	0.40	1595	0.85	1169	2.46	835	1.08	747	1.62
Peak shift between 0.4:1 and 1.0:1 melts	-11		-9		5		8		4		13	
Peak shift between 2.0:1 and 1.0:1 melts	2		3		0		1		3		0	

Table 6  
Comparison of the IR Peak Frequencies of Aluminosy Species

Compound	Peak Frequencies <sup>(1)</sup>	Source
$(\text{Al}_2(\text{H}_2\text{O})_8\text{OH}_2)^{4+}$	3520, 3300, 3130, 2500, 1950, 1080, 980, 790, 730, 630	Ref 24
$\text{H}_2\text{O}$	3490, 1650, 700	Ref 24
$\text{Al}(\text{OH})_3$	3480, 1620, 1010, 760, 530	Sadtler Index Y18K
$\text{Al}_2\text{O}_3$	700, 450	" Y175K
1.6:1 $\text{AlCl}_3/\text{ImCl} + \text{H}_2\text{O}$	3323, 1118, 703	This work
1.6:1 $\text{AlCl}_3/\text{ImCl} + \text{D}_2\text{O}$	2477(0.75), 853(0.76), 662(0.94)	"
0.4:1 $\text{AlCl}_3/\text{ImCl} + \text{H}_2\text{O}$	3520, 3360, 3100, 2410, 2170, 2050, 1170, 1180	"
0.4:1 $\text{AlCl}_3/\text{ImCl} + \text{D}_2\text{O}$	2423(0.72), 2265(0.73)	"

(1) Figures in brackets are the ratio of the peak frequency in  $\text{H}_2\text{O}$  to the frequency in  $\text{D}_2\text{O}$

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#### CREDIT

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### FIGURE CAPTIONS

1. Configuration of IR cell.
2. IR spectrum of empty cell with parallel windows (full line) and with tilted windows (dotted line).
3. Titled cell window configuration.
4. IR spectrum of empty cell (full line) and with 0.8:1  $\text{AlCl}_3/\text{BuPyCl}$  melt (dotted line). Data unsmoothed.
5. IR spectrum of 0.8:1 (full line) and 2.0:1 (dotted line)  $\text{AlCl}_3/\text{BuPyCl}$  melts. Data unsmoothed.
6. IR spectrum of a) 0.8:1 and b) 1.8:1  $\text{AlCl}_3/\text{BuPyCl}$  melts. Data unsmoothed.
7. IR spectrum of 0.8:1, 1.2:1 and 2:1  $\text{AlCl}_3/\text{BuPyCl}$  melts. Data unsmoothed.
8. IR spectrum of 0.4:1 (dotted line) and 1.5:1 (full line)  $\text{AlCl}_3/\text{ImCl}$  melts. Data unsmoothed.
9. Superimposition of 1:1, 1.2:1, 1.5:1 and 1.75:1  $\text{AlCl}_3/\text{ImCl}$  melts. 11 point data smoothing.
10. IR spectrum of 0.4:1, 0.55:1, 0.7:1, 0.85:1 and 0.95:1  $\text{AlCl}_3/\text{ImCl}$  melts. 11 data point smooth.
11. IR spectrum of 0.4:1 (solid line) and 1.5:1 (dashed line)  $\text{AlCl}_3/\text{ImCl}$  melts. Data unsmoothed.
12. IR spectrum of 0.4:1, 0.70:1, 0.95:1 and 1.5:1  $\text{AlCl}_3/\text{ImCl}$  melts. 11 point data smooth.

13. IR spectrum of 1.6:1  $\text{AlCl}_3/\text{ImCl}$  melt after the addition of water (20 mM) and subtraction of a reference 1.6:1  $\text{AlCl}_3/\text{ImCl}$  melt. 11 point data smooth.
14. IR spectrum of a 1.6:1  $\text{AlCl}_3/\text{ImCl}$  melt after the addition of  $\text{D}_2\text{O}$  (60 mM) and subtraction of a reference 1.6:1  $\text{AlCl}_3/\text{ImCl}$  melt. 11 point data smooth.

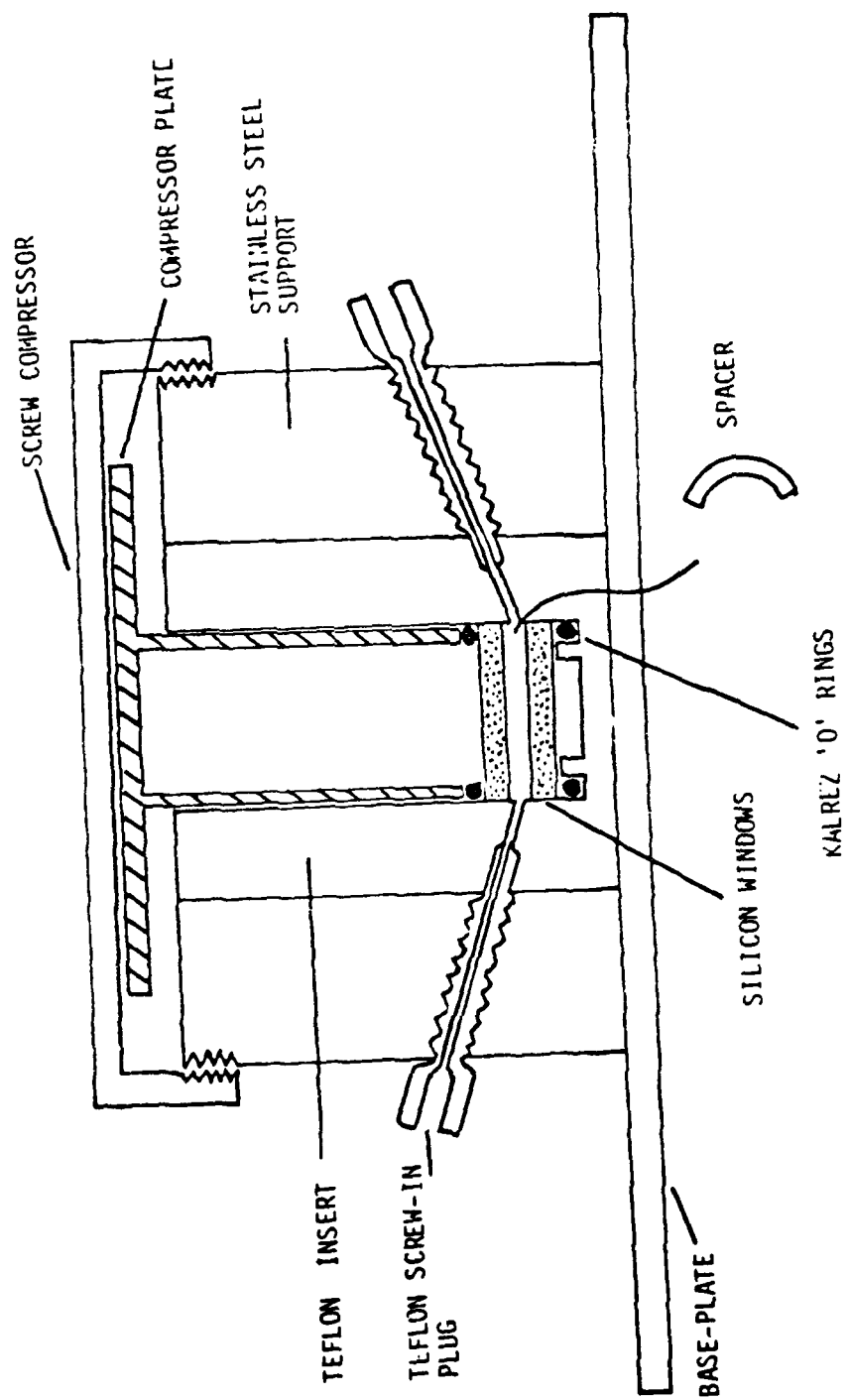


Figure 1

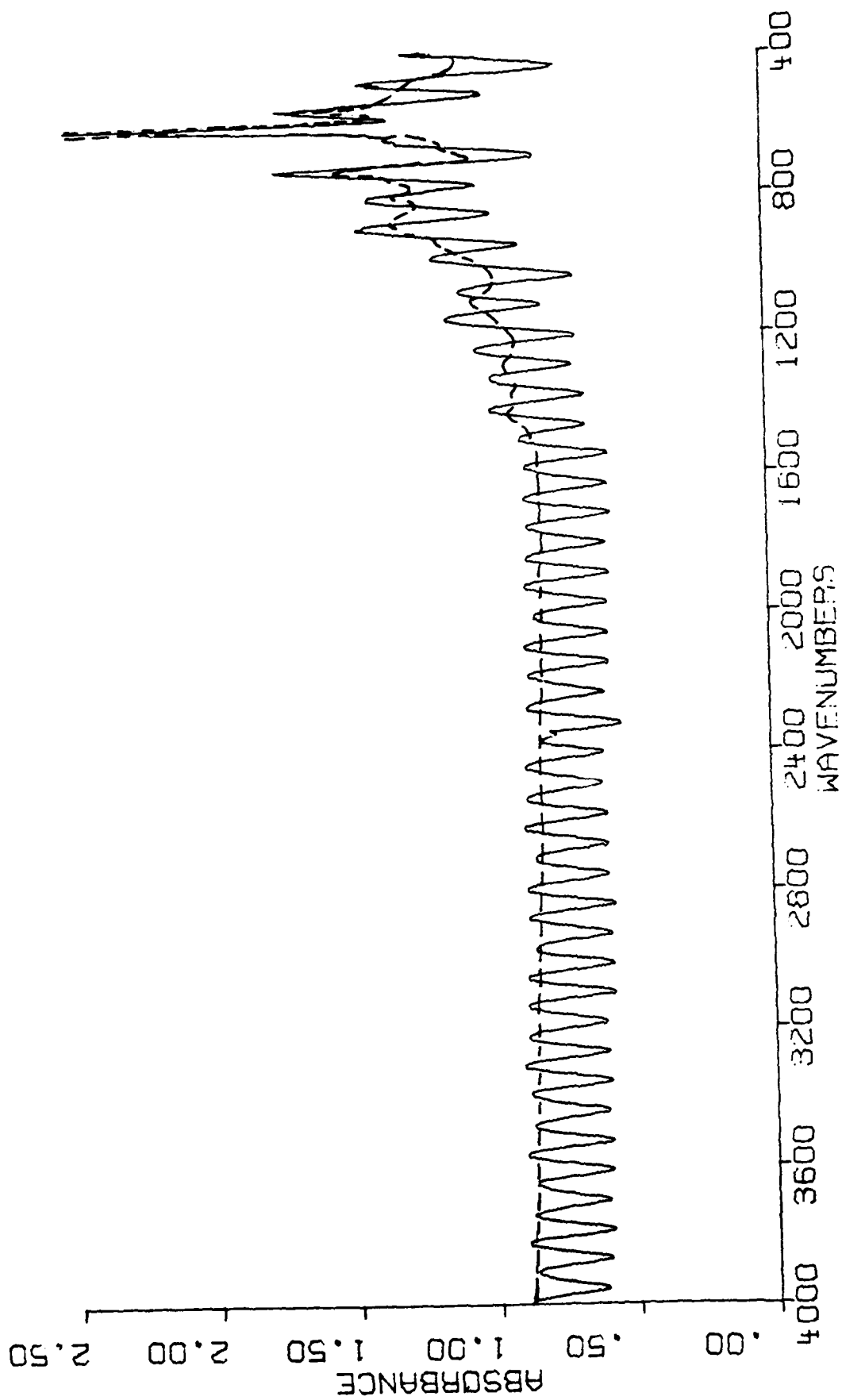


Figure 2

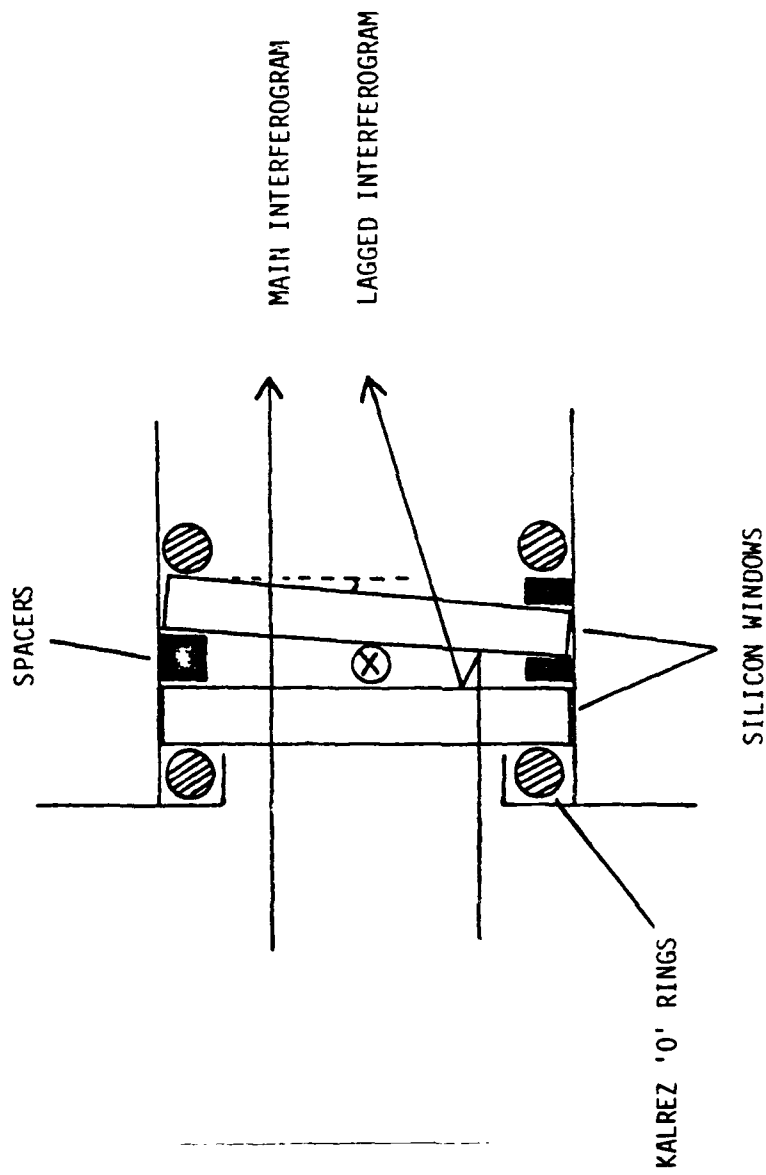


Figure 3

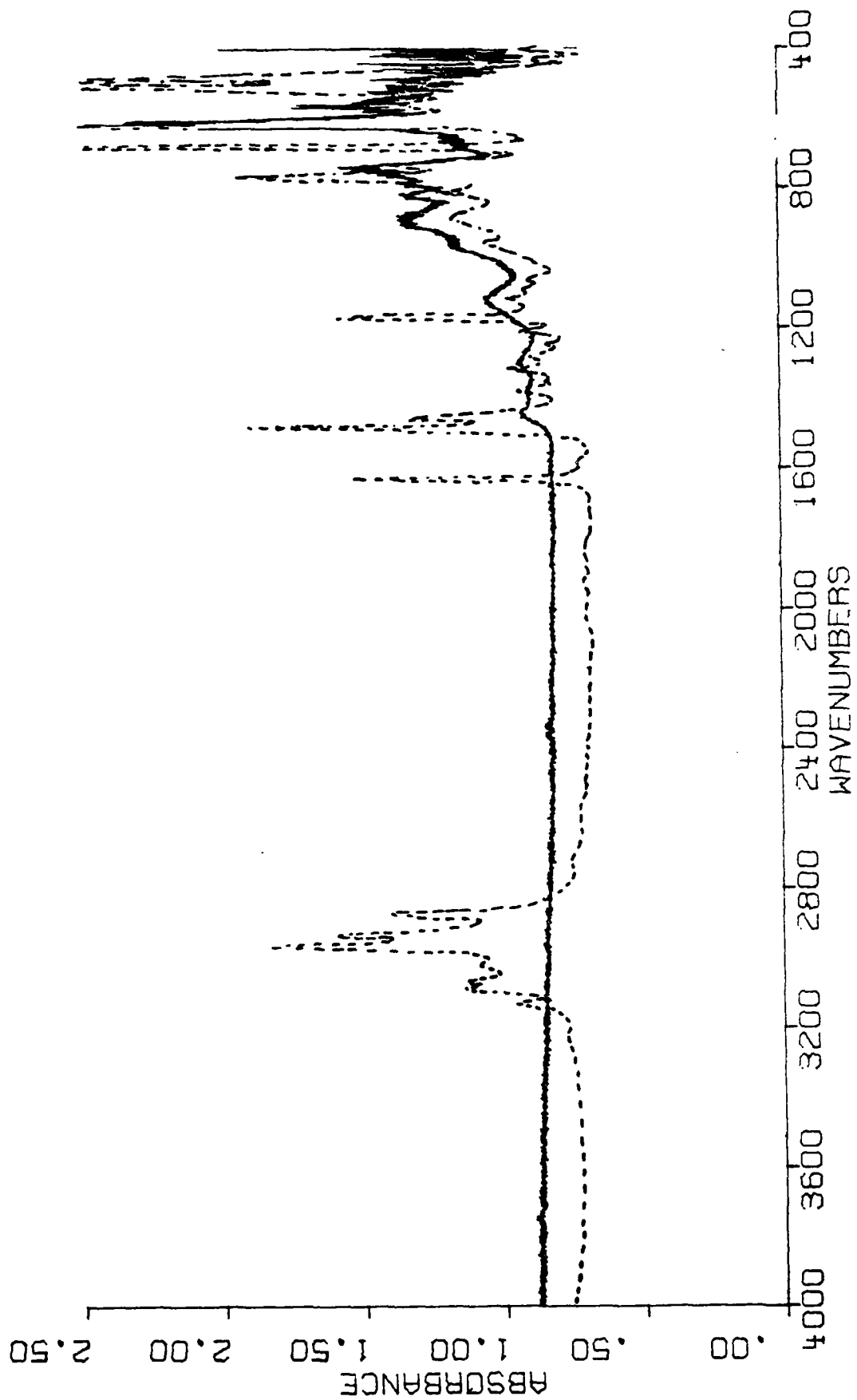


Figure 4



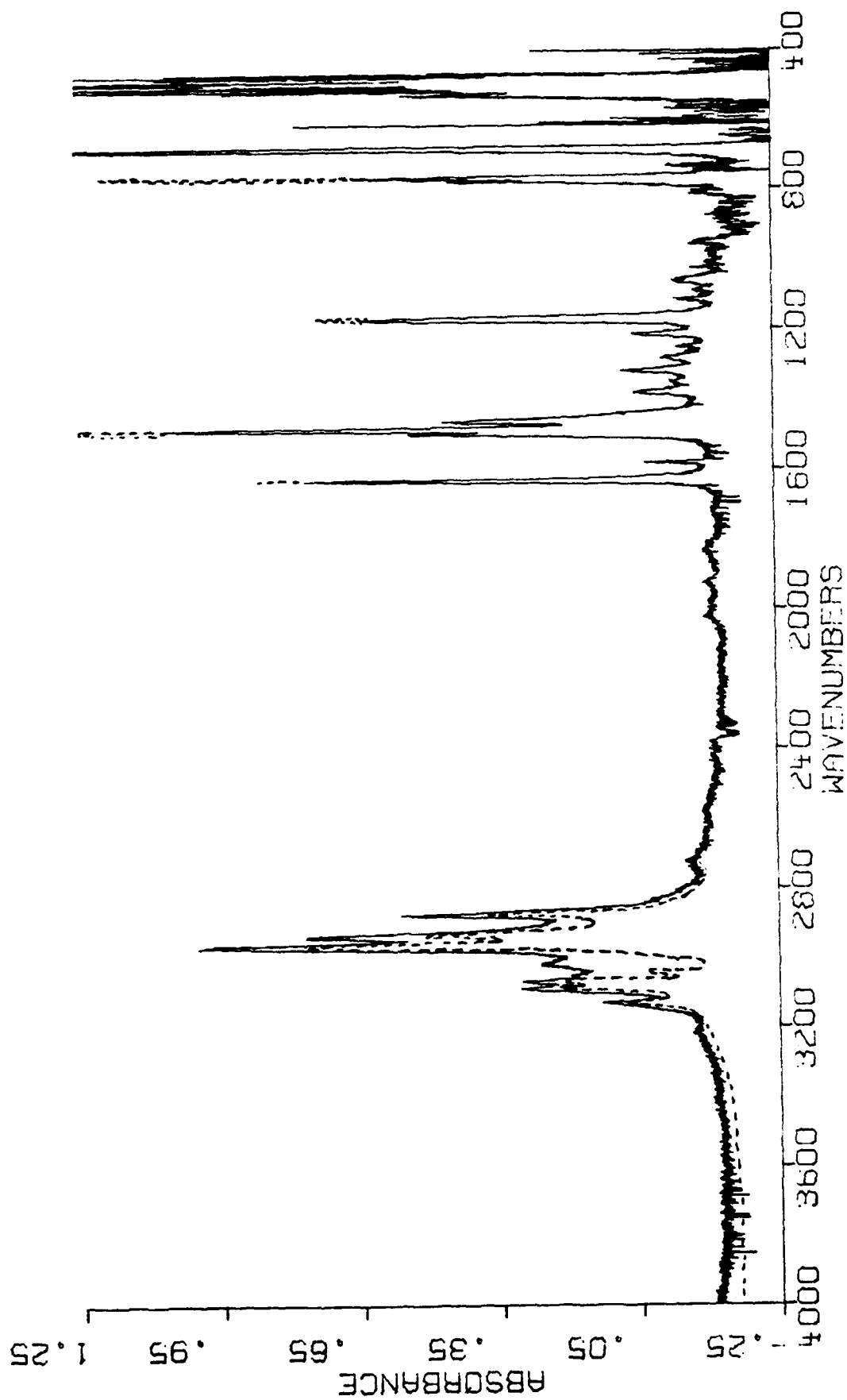


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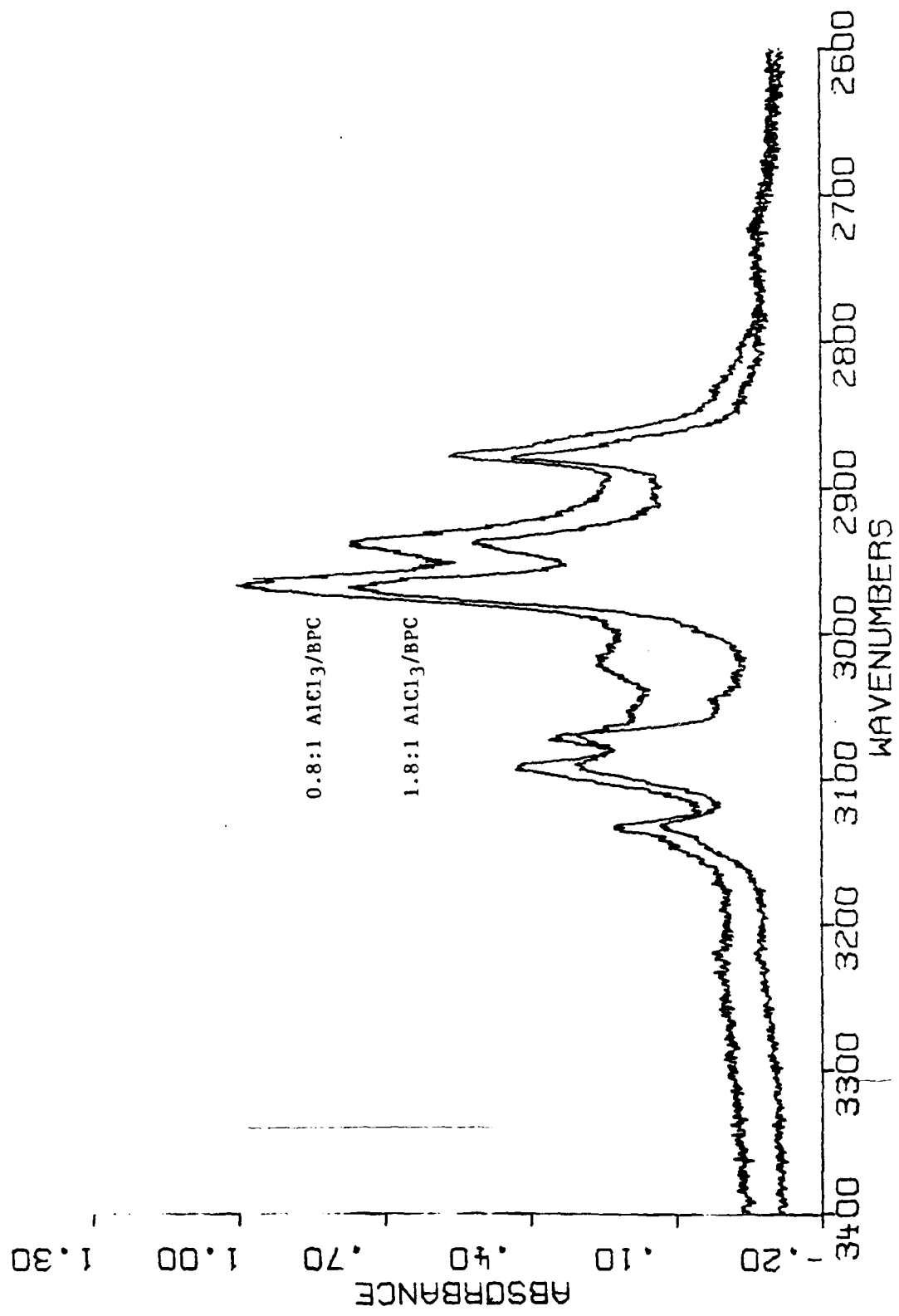


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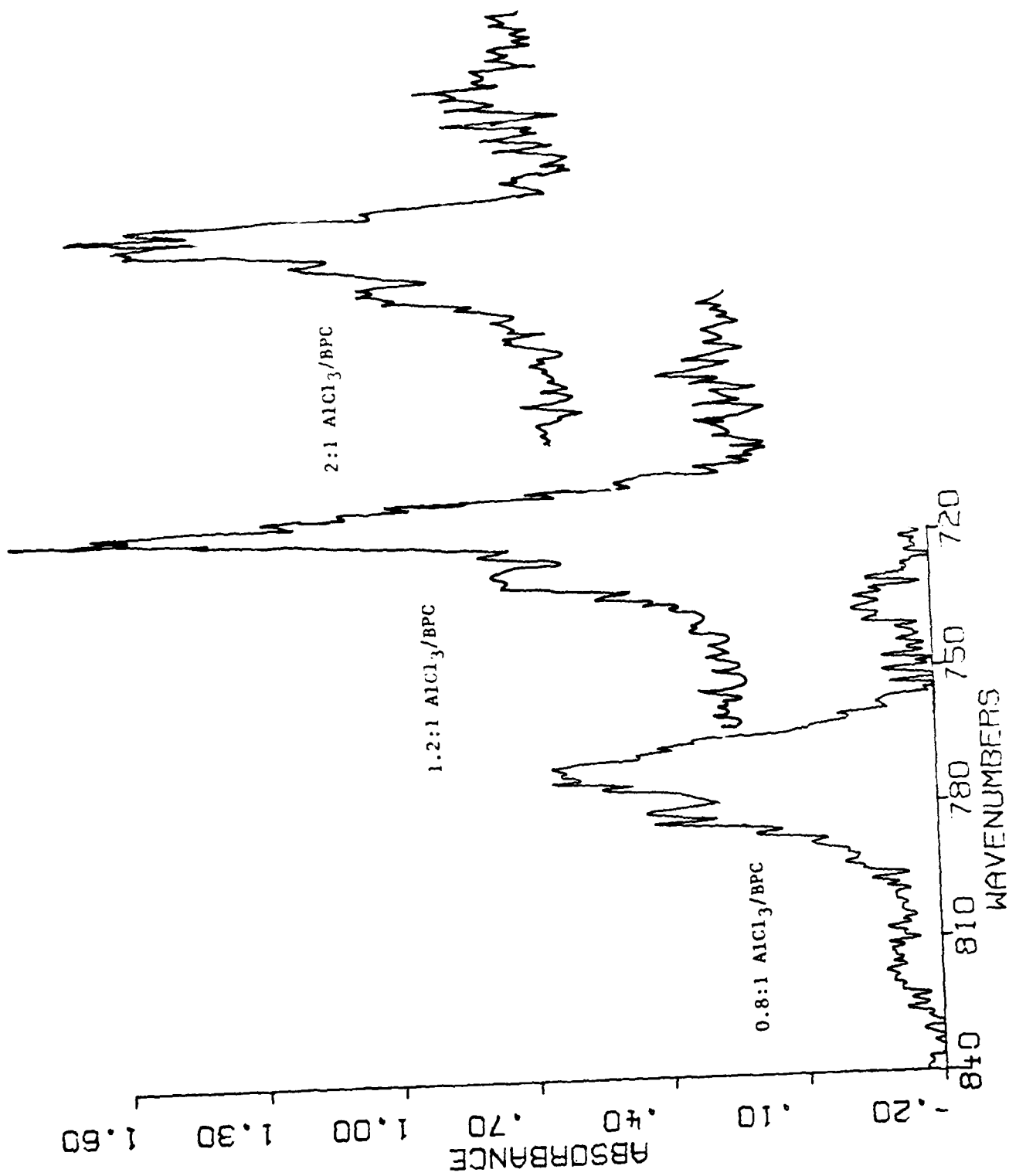


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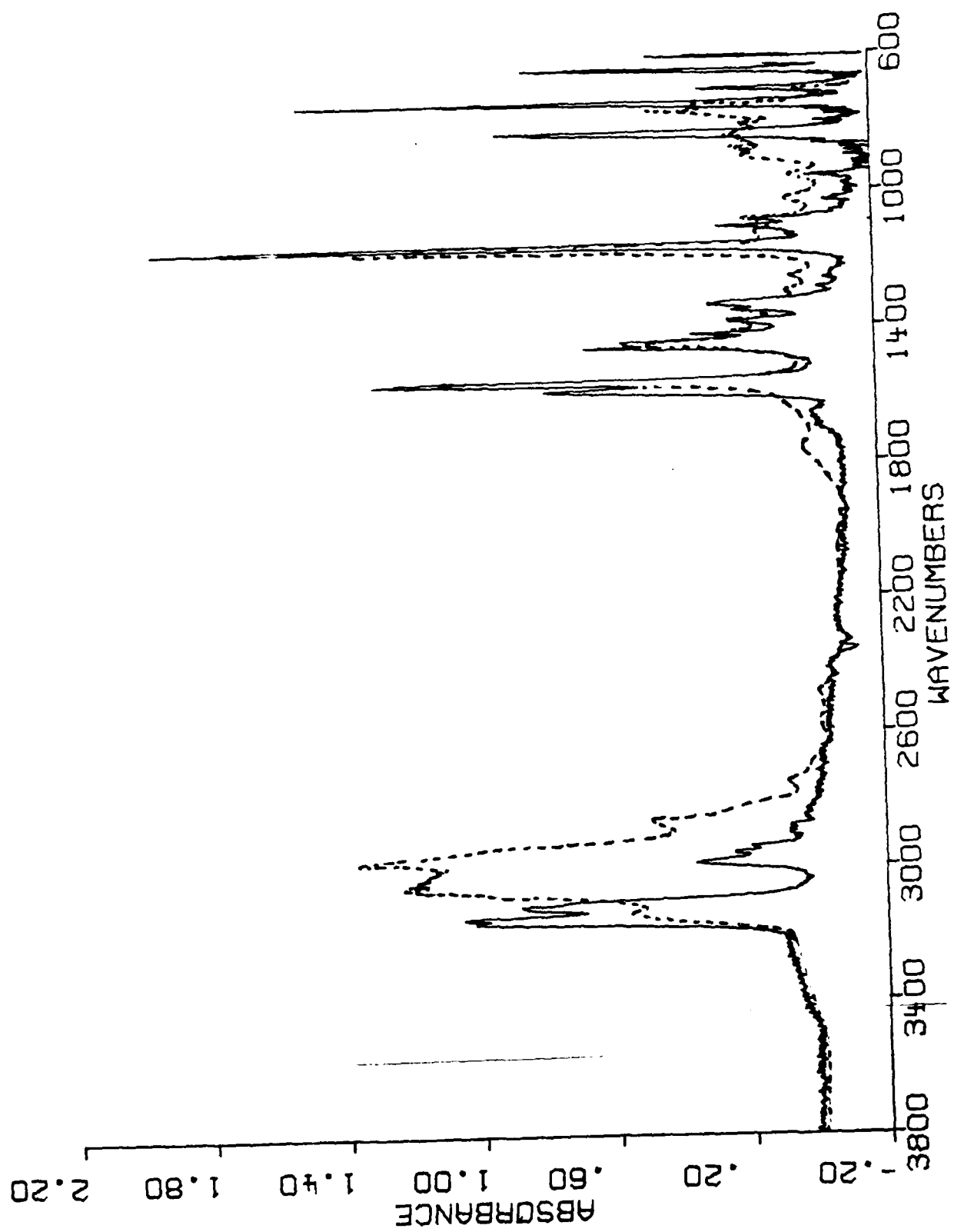


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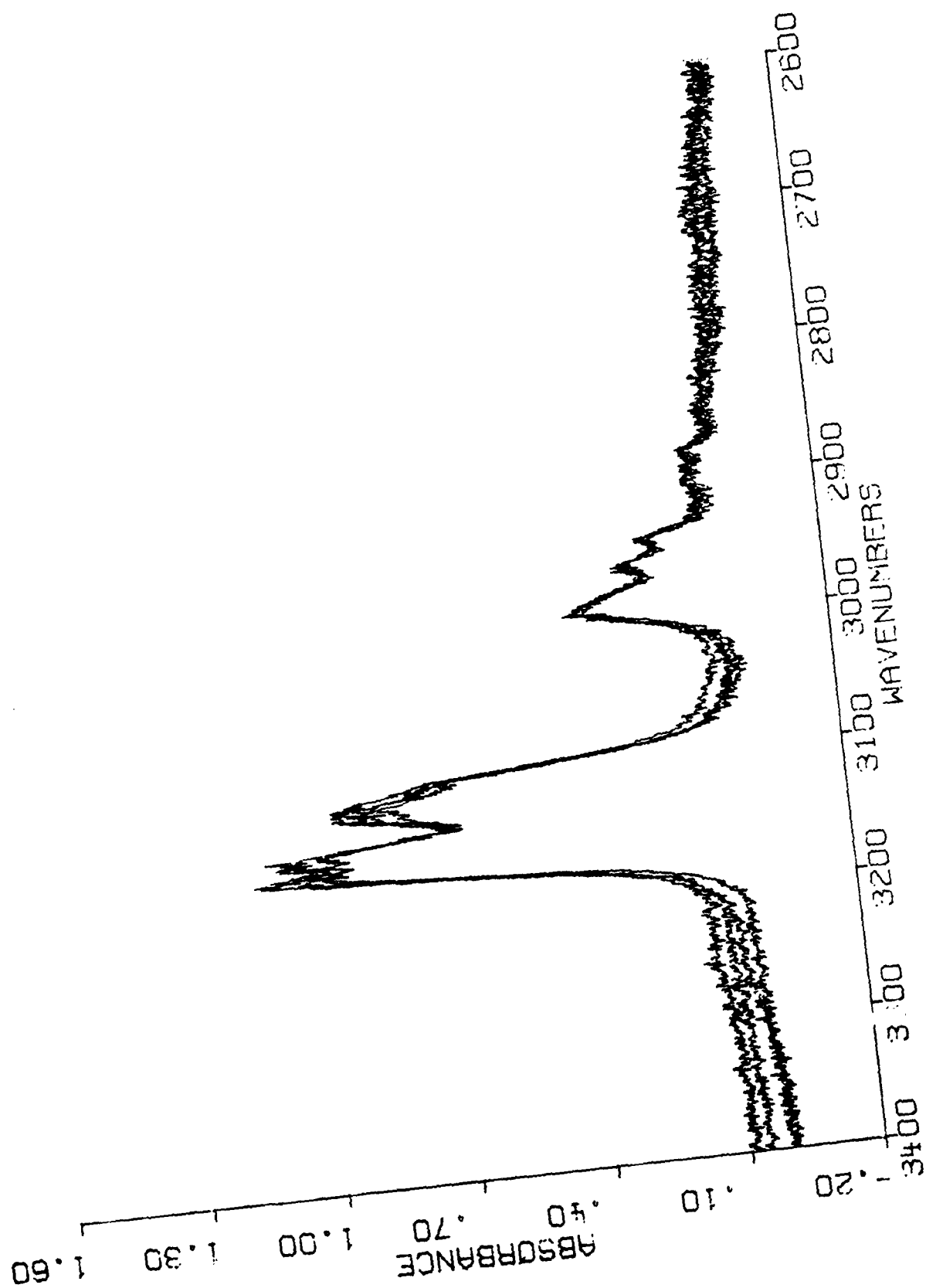


Figure 9

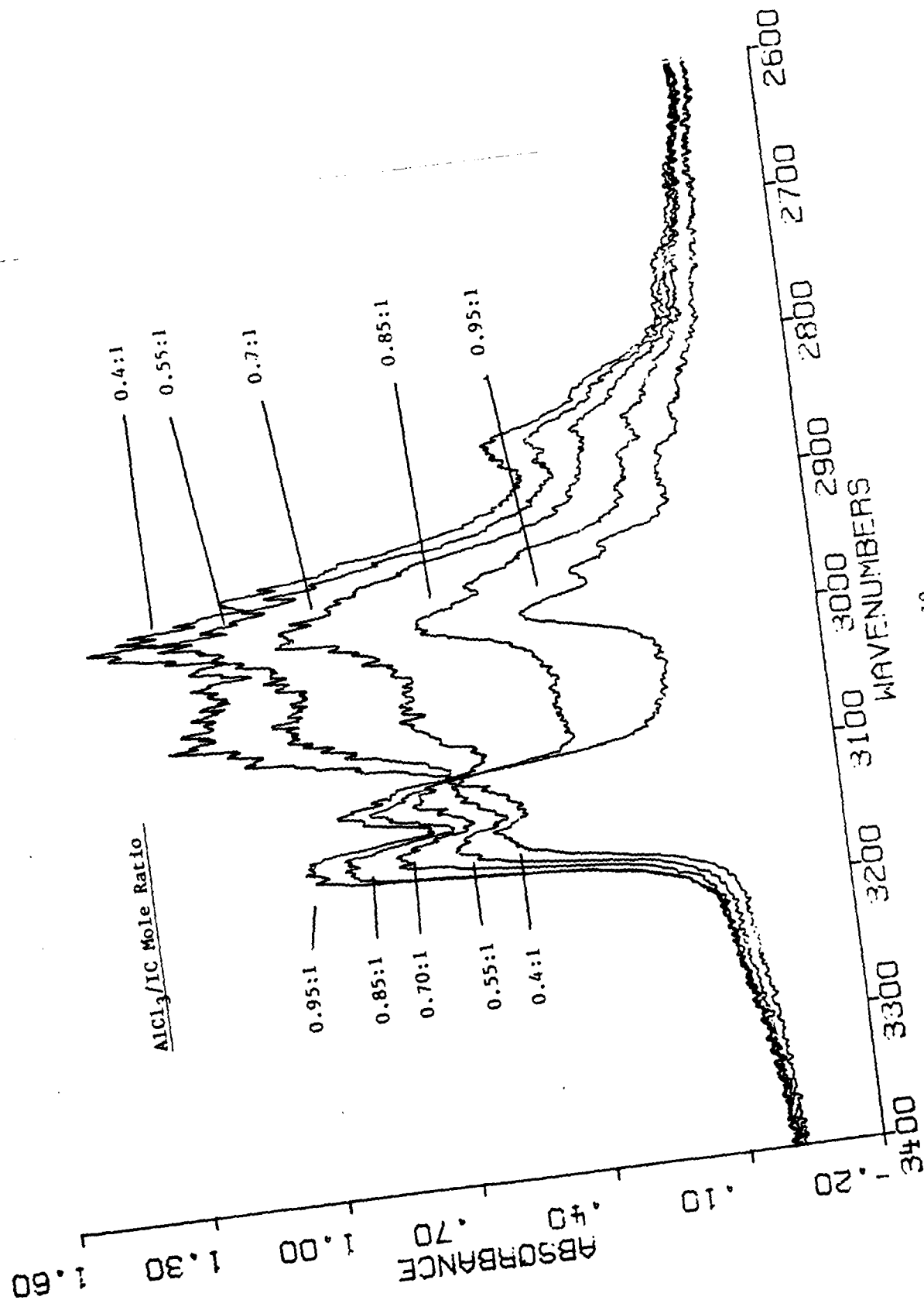


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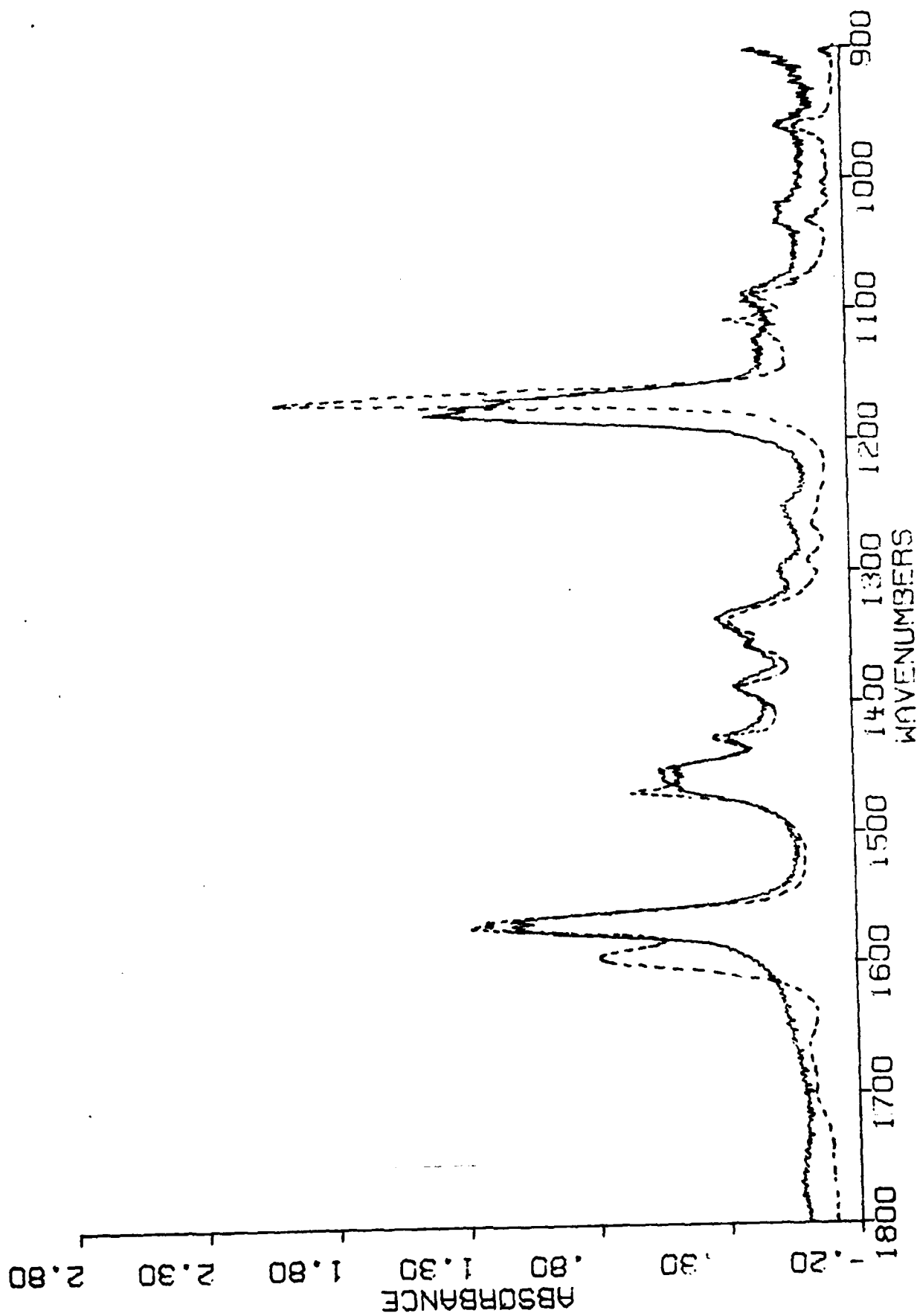


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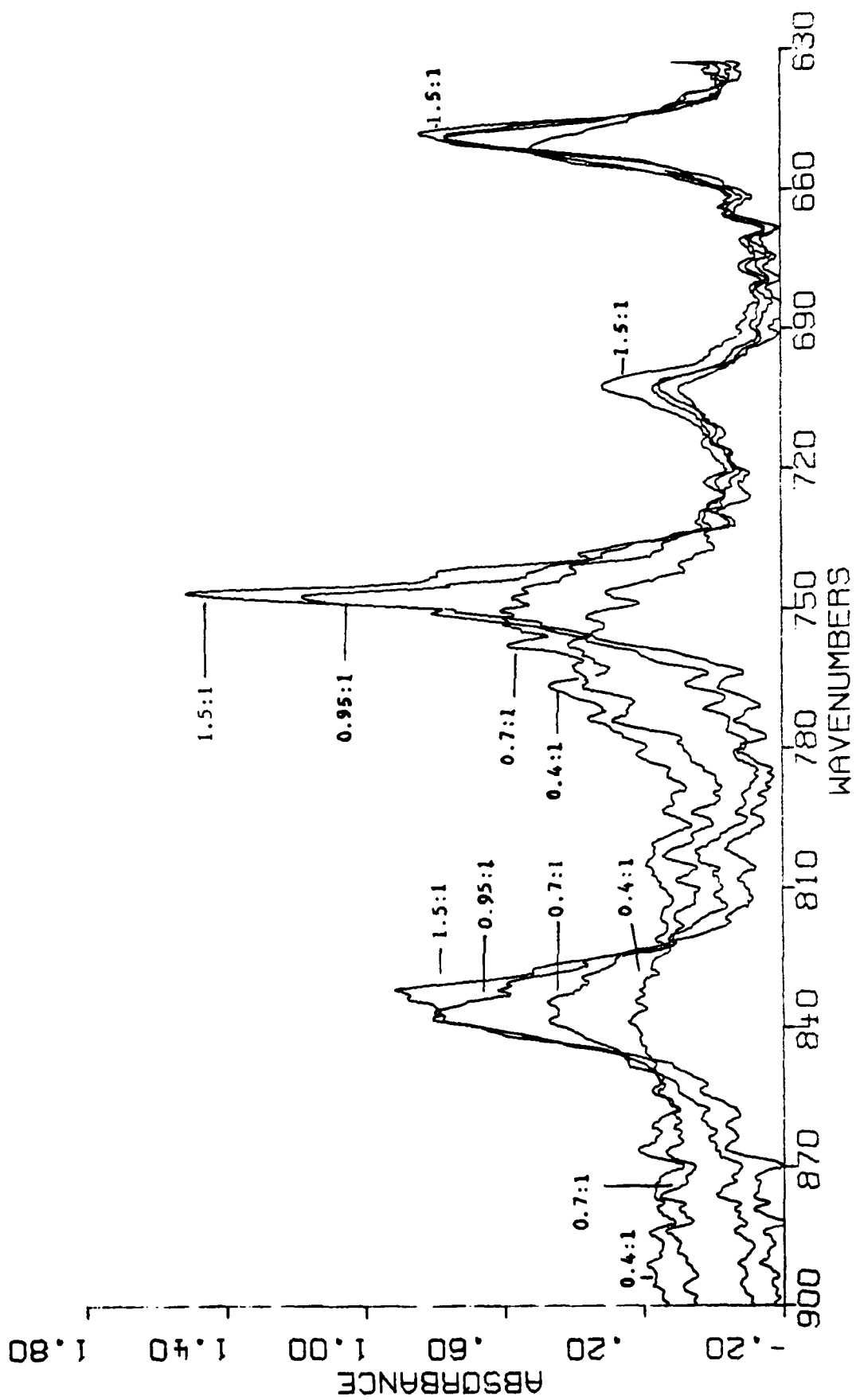


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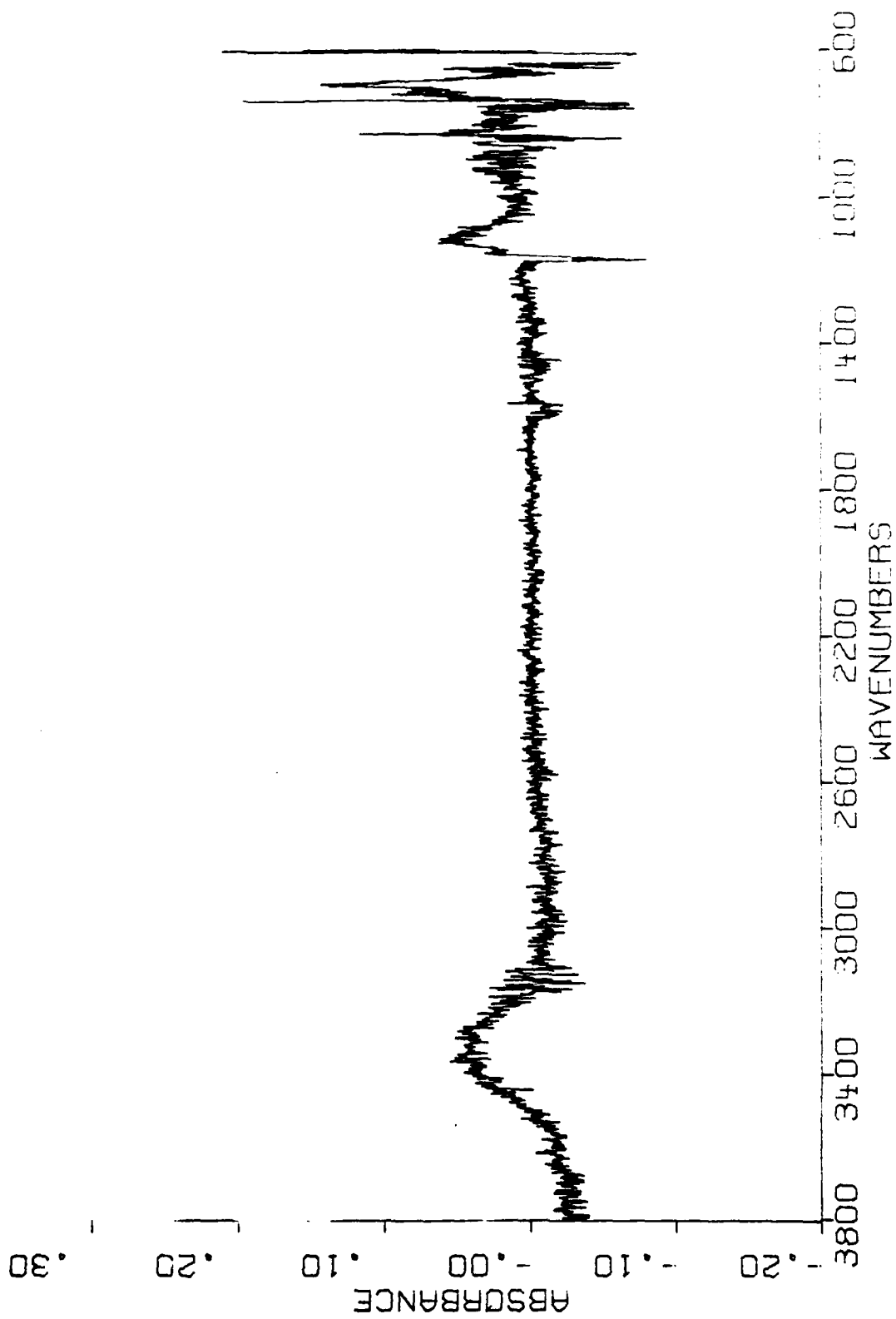


Figure 13

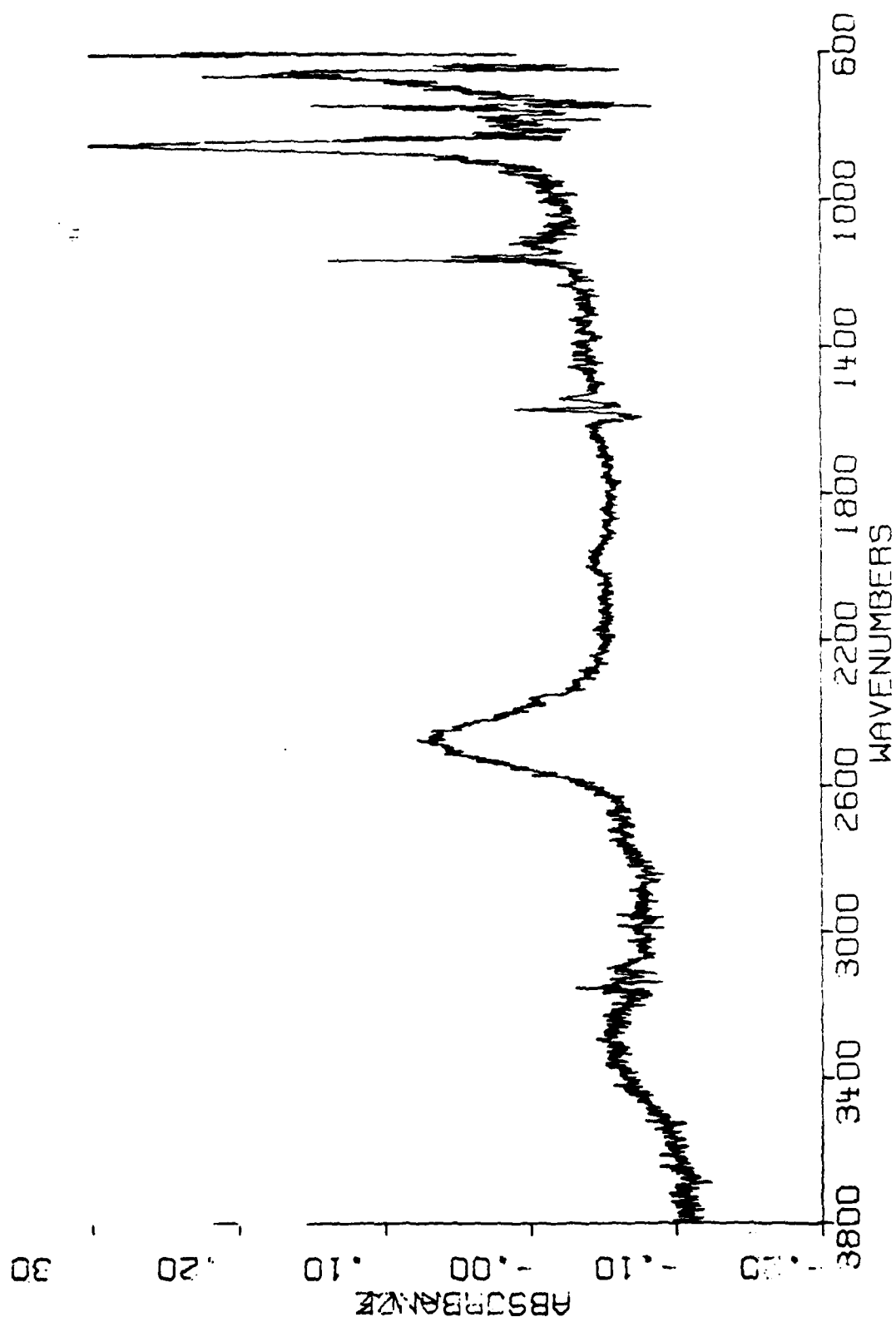


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